

# Ground-state densities from the Rayleigh–Ritz variation principle and from density-functional theory

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The relationship between the densities of ground-state wave functions (i.e., the minimizers of the Rayleigh–Ritz variation principle) and the ground-state densities in density-functional theory (i.e., the minimizers of the Hohenberg–Kohn variation principle) is studied within the framework of convex conjugation, in a generic setting covering molecular systems, solid-state systems, and more. Having introduced admissible density functionals as functionals that produce the exact ground-state energy for a given external potential by minimizing over densities in the Hohenberg–Kohn variation principle, necessary and sufficient conditions on such functionals are established to ensure that the Rayleigh–Ritz ground-state densities and the Hohenberg–Kohn ground-state densities are identical. We apply the results to molecular systems in the Born–Oppenheimer approximation. For any given potential  $v \in L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$ , we establish a one-to-one correspondence between the mixed ground-state densities of the Rayleigh–Ritz variation principle and the mixed ground-state densities of the Hohenberg–Kohn variation principle when the Lieb density-matrix constrained-search universal density functional is taken as the admissible functional. A similar one-to-one correspondence is established between the pure ground-state densities of the Rayleigh–Ritz variation principle and the pure ground-state densities obtained using the Hohenberg–Kohn variation principle with the Levy–Lieb pure-state constrained-search functional. In other words, all physical ground-state densities (pure or mixed) are recovered with these functionals and no false densities (i.e., minimizing densities that are not physical) exist. The importance of topology (i.e., choice of Banach space of densities and potentials) is emphasized and illustrated. The relevance of these results for current-density-functional theory is examined. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4934797>]

## I. INTRODUCTION

The concept of modeling an electron gas and more generally all electronic systems using only the density  $\rho$  goes back to the early days of quantum mechanics and the independent work of Tomas<sup>1</sup> and Fermi<sup>2</sup> in 1927. However, it was only with the seminal work of Hohenberg and Kohn in 1964 that density-functional theory (DFT) was shown to be—in principle, at least—an exact theory.<sup>3</sup> In 1983, Lieb formulated DFT rigorously for electronic systems in  $\mathbb{R}^3$ , using concepts from convex analysis.<sup>4</sup> Today, DFT is the most popular computational method for many-electron systems in chemistry and solid-state physics.

In an external electrostatic scalar potential  $v$ , the ground-state energy  $E(v)$  of an  $N$ -electron system is obtained from the Rayleigh–Ritz variation principle

$$E(v) := \inf_{\psi} \langle \psi | \hat{H}(v) | \psi \rangle, \quad (1)$$

where  $\hat{H}(v)$  is the Hamiltonian and the infimum extends over all  $L^2$ -normalized wave functions for which the expectation value makes sense. With each minimizing ground-state wave

function  $\psi$  in Eq. (1), there is an associated ground-state density  $\rho$ . In DFT, the ground-state energy  $E(v)$  is instead obtained from the Hohenberg–Kohn variation principle,

$$E(v) = \inf_{\rho} (F_0(\rho) + (v|\rho)), \quad (2)$$

where  $F_0(\rho)$  is a *universal functional* and the minimization is over all densities for which the interaction  $(v|\rho) = \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$  is meaningful. Note that we have not specified the spatial domain nor the nature of the external potential  $v$ . Thus, minimization problems Eqs. (1) and (2) are so far not fully defined from a mathematical perspective. Moreover, the functional  $F_0$  is not unique—any functional  $F_0$  that gives the correct ground-state energy in the Hohenberg–Kohn variation principle is said to be “admissible.” Common expositions of DFT use the Levy–Lieb constrained-search functional  $F_{LL}$ ,<sup>4,5</sup> the density-matrix constrained-search functional  $F_{DM}$ ,<sup>4</sup> and the Lieb functional  $F$ , all giving the same ground-state energy  $E(v)$  for a large class of potentials. Specializing to electrons in  $\mathbb{R}^3$  and assuming that the external potential  $v$  is sufficiently well behaved, these functionals are given by the following expressions:

$$F_{LL}(\rho) := \inf \{ \langle \psi | \hat{H}_0 | \psi \rangle | \psi \in H_S^1(\mathbb{R}^{3N}), \|\psi\|_2 = 1, \psi \mapsto \rho \}, \quad (3)$$

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$$F_{\text{DM}}(\rho) := \inf \left\{ \text{Tr}(\hat{H}_0 \Gamma) \mid \Gamma = \sum_k \lambda_k |\psi_k\rangle\langle\psi_k|, \sum_k \lambda_k = 1, \right. \\ \left. \lambda_k \geq 0, \psi_k \in H_S^1(\mathbb{R}^{3N}), \|\psi_k\|_2 = 1, \Gamma \mapsto \rho \right\}, \quad (4)$$

$$F(\rho) := \sup_{v \in X'} (E(v) - (v|\rho)). \quad (5)$$

Here,  $H_S^1(\mathbb{R}^{3N})$  is the first-order Sobolev space  $H^1(\mathbb{R}^{3N})$  with proper permutation symmetry due to spin,  $\hat{H}_0 = \hat{T} + \hat{W}$  is the sum of the kinetic and inter-electron interaction operators, and  $\psi \mapsto \rho$  and  $\Gamma \mapsto \rho$  indicate that the wave function  $\psi$  and density matrix  $\Gamma$ , respectively, have density  $\rho$ . In the definition of the Lieb functional,  $X$  is a Banach space in which densities are embedded, with  $X'$  as its dual, consisting of potentials. (A Banach space is a normed vector space that is complete, meaning that each Cauchy sequence converges to an element of that space.) We note that the Lieb functional is by construction lower semi-continuous and convex, being the conjugate function to  $E$  in the sense of convex analysis.

Although the density functionals  $F_{\text{LL}}$ ,  $F_{\text{DM}}$ , and  $F$  are all admissible with the same total energy in the Hohenberg–Kohn variation principle, they may have different minimizing densities. In this article, we study the relationship between the densities in the Hohenberg–Kohn and Rayleigh–Ritz variation principles. In particular, we establish what conditions must be imposed on an admissible density functional to ensure that the ground-state densities (i.e., the minimizing densities) in the Hohenberg–Kohn variation principle are the same as the densities of the ground-state wave functions (i.e., the minimizing wave functions) in the Rayleigh–Ritz variation principle.

While our treatment covers the standard DFT setting outlined above, it is motivated by a study of current-density-functional theory (CDFT), where the  $N$ -electron system is subject to an external magnetic vector potential  $\mathbf{A}$  in addition to the scalar potential  $v$ ,<sup>6–8</sup> introducing the paramagnetic current density  $\mathbf{j}_p \in \mathbf{L}^1(\mathbb{R}^3)$  as an additional variable in the Hohenberg–Kohn variation principle,

$$E(v, \mathbf{A}) = \inf_{\rho, \mathbf{j}_p} (F_0(\rho, \mathbf{j}_p) + (v + \frac{1}{2}A^2|\rho) + (\mathbf{A}|\mathbf{j}_p)), \quad (6)$$

where  $(\mathbf{A}|\mathbf{j}_p) = \int \mathbf{A}(\mathbf{r}) \cdot \mathbf{j}_p(\mathbf{r}) \, d\mathbf{r}$ . The CDFT generalization of the Levy–Lieb functional is the *Vignale–Rasolt (VR) functional*  $F_{\text{VR}}(\rho, \mathbf{j}_p)$ ; there is likewise a generalization of the density-matrix constrained-search functional  $F_{\text{DM}}$  and the Lieb functional  $F$  to include a current dependence. The mathematical properties of these functionals are not as well understood as the functionals that appear in the standard DFT setting. The results presented in this article are in part meant to be a step towards such an understanding.

The article is structured as follows. In Sec. II, we describe DFT from a generic and abstract point of view, introducing arbitrary admissible density functionals  $F_0$  and some concepts of convex analysis. We obtain several results that characterize the relationship between minimizers of the Rayleigh–Ritz variation principle and of the Hohenberg–Kohn variation principle. In Sec. III, we apply our findings to the standard DFT of atoms and molecules in the Born–Oppenheimer approximation. The importance of the topology of the underlying density space is emphasized. In Sec. IV, we discuss CDFT, and finally, in Sec. V, we summarize and draw some conclusions.

## II. DFT FROM AN ABSTRACT POINT OF VIEW

### A. Admissible universal density functionals

Except for the trivial case of one electron, an explicit formula for any of the standard density functionals used in the Hohenberg–Kohn variation principle in Eq. (2) is not known. Moreover, the mathematical analysis of Eq. (2) is difficult without further assumptions. In his work,<sup>4</sup> Lieb placed DFT for electronic systems in  $\mathbb{R}^3$  on a firm mathematical ground using the language of *convex analysis*,<sup>9,10</sup> the natural setting for problems such as Eq. (2). The starting point is to embed the densities in a Banach space  $X$  and to consider potentials in the dual space  $X'$ , thereby making the interaction  $(v|\rho)$  well-defined and continuous in both arguments. We then obtain the ground-state energy as a map  $E : X' \rightarrow \mathbb{R} \cup \{-\infty\}$  given by

$$E(v) = \inf_{\rho \in X} (F_0(\rho) + (v|\rho)), \quad \forall v \in X', \quad (7)$$

where  $F_0 : X \rightarrow \mathbb{R} \cup \{+\infty\}$  is the universal density functional. Being the pointwise infimum of a collection of affine maps of the form  $v \mapsto (v|\rho) + F_0(\rho)$ , the ground-state energy in Eq. (7) is automatically *concave and upper semi-continuous* with respect to the topology on  $X'$ . Note that we allow  $E$  and  $F_0$  to be infinite. The *effective domain* of a function is the set where the function is finite—for example,  $\text{dom}(E) = \{v \in X' \mid E(v) > -\infty\}$ .

In Ref. 4, Lieb (and Simon) proved several important results in the context where  $X = L^1(\mathbb{R}^3) \cap L^3(\mathbb{R}^3)$  (consisting of all functions contained in both  $L^1(\mathbb{R}^3)$  and  $L^3(\mathbb{R}^3)$ ), with dual  $X' = L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$  (consisting of all sums of functions in  $X' = L^{3/2}(\mathbb{R}^3)$  and  $L^\infty(\mathbb{R}^3)$ ). However, this choice of  $X$  is not unique, and the derived results may depend on  $X$ . We emphasize that, even if our notation suggests the standard DFT setting, it covers also CDFT and other settings.

A function  $F_0 : X \rightarrow \mathbb{R} \cup \{+\infty\}$  is said to be an *admissible* density functional if, for each potential  $v \in X'$ , it gives a correct ground-state energy by the Hohenberg–Kohn variation principle in Eq. (7)—that is, if it gives the same energy as does the Rayleigh–Ritz variation principle in Eq. (1). Note that we do not require that there exists a minimizing density  $\rho$  for a given potential  $v$ , even in those cases where  $v$  supports a ground state in the Rayleigh–Ritz variation principle in Eq. (1). It is sufficient that a minimizing sequence  $\{\rho_n\}$  can be found. Clearly, for any pair  $(\rho, v) \in X \times X'$ , an admissible density functional and the ground-state energy satisfy the *Fenchel inequality*

$$E(v) \leq F_0(\rho) + (v|\rho). \quad (8)$$

We are here interested in characterizing those pairs  $(\rho, v)$  that saturate Fenchel's inequality,  $E(v) = F_0(\rho) + (v|\rho)$ , in other words, those  $\rho \in X$  that are minimizers in Eq. (7) for a given  $v \in X'$ .

Since the universal functional is, in general, not differentiable (see Refs. 4 and 11 for the standard DFT case), we cannot write down an Euler equation for the solution of the minimization problem Eq. (7). Moreover, even if  $F_0$  were differentiable, the Euler equation would, in general, be a necessary but not sufficient condition for a global minimum in Eq. (7). Instead, we use the concept of *subdifferentiation* to characterize the

solution. The admissible density functional  $F_0$  is said to be *subdifferentiable* at  $\rho \in X$  if  $F_0(\rho) \in \mathbb{R}$  and if there exists  $u \in X'$ , known as a *subgradient* of  $F_0$  at  $\rho$ , such that

$$F_0(\rho') \geq F_0(\rho) + (u|\rho' - \rho), \quad \forall \rho' \in X, \quad (9)$$

$$\partial^- F_0(\rho) = \{u \in X' | F_0(\rho') \geq F_0(\rho) + (u|\rho' - \rho), \forall \rho' \in X, F_0(\rho) \in \mathbb{R}\}. \quad (10)$$

This set is convex.<sup>9</sup> Note that the subdifferential is the empty set whenever  $F_0(\rho) = +\infty$ . Assuming that  $-v$  is a subgradient of  $F_0$  at  $\rho$ , we obtain by simple rearrangements

$$\begin{aligned} -v \in \partial^- F_0(\rho) & \\ \iff F_0(\rho') &\geq F_0(\rho) + (-v|\rho' - \rho) \\ \iff F_0(\rho) + (v|\rho) &\leq F_0(\rho') + (v|\rho') \\ \iff F_0(\rho) + (v|\rho) &= \inf_{\rho' \in X} (F_0(\rho') + (v|\rho')) = E(v). \end{aligned} \quad (11)$$

We have thus shown the following sufficient and necessary condition for a minimizing density in the Hohenberg–Kohn variation principle in Eq. (7):

*Proposition 1.* Let  $F_0 : X \rightarrow \mathbb{R} \cup \{+\infty\}$  be an admissible density functional so that Eq. (7) holds. Let  $v \in X'$  and  $\rho \in X$  be given. Then,

$$E(v) = F_0(\rho) + (v|\rho) \iff -v \in \partial^- F_0(\rho). \quad (12)$$

## B. Lieb's universal density functional

From the Fenchel inequality in Eq. (8), we obtain by a trivial rearrangement the equivalent inequality

$$F_0(\rho) \geq E(v) - (v|\rho), \quad (13)$$

stating that each admissible density functional  $F_0(\rho)$  is an upper bound to  $\rho \mapsto E(v) - (v|\rho)$  with respect to all variations in  $\rho \in X$ . We now define the *Lieb universal density functional*  $F(\rho)$  as the *least upper bound* to  $E(v) - (v|\rho)$  for all  $v \in X'$ ,

$$F(\rho) := \sup_{v \in X'} (E(v) - (v|\rho)), \quad \forall \rho \in X, \quad (14)$$

which in the following will be referred to as the *Lieb variation principle*. The Lieb functional is clearly a lower bound to all admissible density functionals,

$$F(\rho) \leq F_0(\rho). \quad (15)$$

Since the Lieb functional by construction also satisfies the Fenchel inequality in Eq. (8), we obtain the following:

*Proposition 2.* The Lieb functional is an admissible density functional

$$E(v) = \inf_{\rho \in X} (F(\rho) + (v|\rho)), \quad \forall v \in X'. \quad (16)$$

*Proof.*  $E(v) \leq \inf_{\rho \in X} (F(\rho) + (v|\rho)) \leq \inf_{\rho \in X} (F_0(\rho) + (v|\rho)) = E(v)$ .  $\square$

The Lieb functional is related to the ground-state energy in a special, symmetrical manner—compare the Lieb variation

meaning that  $F_0$  touches the affine map  $\rho' \mapsto F_0(\rho') + (u|\rho' - \rho)$  at  $\rho$  and lies nowhere below it. The subgradient is thus a generalization of the concept of the slope of a tangent to the graph of  $F_0$  at  $\rho$ . The *subdifferential*  $\partial^- F_0(\rho)$  is the (possibly empty) set of all subgradients of  $F_0$  at  $\rho$ ,

principle in Eq. (14) with Hohenberg–Kohn variation principle equation (16). In the language of convex analysis,  $E$  and  $F$  are said to be *skew conjugate functions*:<sup>12</sup> the function  $E$  is concave and upper semi-continuous, whereas its skew conjugate function  $F$  is convex and lower semi-continuous. Convexity of  $F$  and concavity of  $E$  mean that, for each pair  $\rho_1, \rho_2 \in X$ , each pair  $v_1, v_2 \in X'$ , and each  $\lambda \in (0, 1)$ , we have

$$F(\lambda\rho_1 + (1 - \lambda)\rho_2) \leq \lambda F(\rho_1) + (1 - \lambda)F(\rho_2), \quad (17)$$

$$E(\lambda v_1 + (1 - \lambda)v_2) \geq \lambda E(v_1) + (1 - \lambda)E(v_2), \quad (18)$$

whereas lower semi-continuity of  $F$  and upper semi-continuity of  $E$  imply that

$$\liminf_{\rho \rightarrow \rho_0} F(\rho) \geq F(\rho_0), \quad (19)$$

$$\limsup_{v \rightarrow v_0} E(v) \leq E(v_0). \quad (20)$$

These properties follow straightforwardly from Eqs. (14) and (16). It is a fundamental result of convex analysis that *there is a one-to-one correspondence between all lower semi-continuous convex functions on  $X$  and all upper semi-continuous concave functions on  $X'$* ,<sup>9,10,12</sup> the correspondence being as in Eqs. (14) and (16). It follows that the Lieb functional  $F$  is not only a lower bound to all admissible density functionals but also the *only admissible density functional that is lower semi-continuous and convex with respect to the topology on  $X$* . It is a trivial but important observation that each property and each feature of  $E$  are, in some manner, exactly reflected in the properties and features of  $F$  and vice versa. Note, however, that the Lieb functional depends explicitly on  $X$ , just like  $E$  depends on  $X'$ .

Just like there may happen to be no minimizing density in the Hohenberg–Kohn variation principle, there may happen to be no maximizing potential in the Lieb variation principle. To characterize maximizing potentials, we introduce superdifferentiability by analogy with subdifferentiability. The ground-state energy  $E$  is said to be *superdifferentiable* at  $v \in X'$  if there exists an element  $\rho \in X$ , known as a *supergradient* of  $E$  at  $v$ , such that

$$E(v') \leq E(v) + (v' - v|\rho), \quad \forall v' \in X'. \quad (21)$$

The *superdifferential*  $\partial^+ E(v)$  is the (possibly empty) convex set of all supergradients of  $E$  at  $v$ ,

$$\begin{aligned} \partial^+ E(v) & \\ &= \{\rho \in X | E(v') \leq E(v) + (\rho|v' - v), \forall v' \in X', E(v) \in \mathbb{R}\}. \end{aligned} \quad (22)$$

In exactly the same manner that we proved Eq. (12), we obtain the following necessary and sufficient conditions for the existence of a maximizing potential in the Lieb variation principle:

$$E(v) = F(\rho) + (v|\rho) \iff \rho \in \partial^+ E(v). \quad (23)$$

Note carefully that this result holds only for the Lieb functional, not for an arbitrary admissible density functional. Combining Eqs. (12) and (23), we arrive at the following characterization of the optimality condition in Eqs. (14) and (16):

*Proposition 3.* If  $F : X \rightarrow \mathbb{R} \cup \{+\infty\}$  is the Lieb functional and  $E : X' \rightarrow \mathbb{R} \cup \{-\infty\}$  is the ground-state energy, then

$$E(v) = F(\rho) + (v|\rho) \iff -v \in \partial^- F(\rho) \iff \rho \in \partial^+ E(v). \quad (24)$$

For a general admissible density functional  $F_0$ , the conditions in Eq. (24) are not equivalent: there may exist  $\rho \in \partial^+ E(v)$  such that  $-v \notin \partial^- F_0(\rho)$  when  $F_0 \neq F$ . On the other hand, the converse statement,  $-v \in \partial^- F_0(\rho) \implies \rho \in \partial^+ E(v)$ , holds for any admissible density functional  $F_0$ . To prove this, assume that  $-v \in \partial^- F_0(\rho)$ . According to Eq. (12), we then have  $F_0(\rho) = E(v) - (v|\rho)$ . At the same time, the Fenchel inequality holds for any admissible density functional  $F_0$ ,

$$E(u) \leq F_0(\rho) + (u|\rho), \quad \forall u \in X'. \quad (25)$$

Substituting  $F_0(\rho) = E(v) - (v|\rho)$  in this inequality, we obtain

$$E(u) \leq E(v) + (u - v|\rho), \quad \forall u \in X', \quad (26)$$

implying that  $\rho \in \partial^+ E(v)$ . We have thus proved the following:

*Proposition 4.* If  $F_0 : X \rightarrow \mathbb{R} \cup \{+\infty\}$  is an admissible functional and  $E : X' \rightarrow \mathbb{R} \cup \{-\infty\}$  the ground-state energy, then

$$E(v) = F_0(\rho) + (v|\rho) \iff -v \in \partial^- F_0(\rho) \implies \rho \in \partial^+ E(v). \quad (27)$$

We note that  $E$  (being upper semi-continuous and concave on  $X'$ ) and  $F_0$  (being lower semi-continuous and convex on  $X$ ) are superdifferentiable and subdifferentiable, respectively, on dense subsets of their domains. These are general results of convex analysis (the Brøndsted–Rockafellar and Bishop–Phelps theorems) but were first noted in the context of DFT by Lieb.<sup>4</sup>

In general, we have  $F \leq F_0$ . However, according to the following proposition, an admissible density functional  $F_0(\rho)$  can differ from  $F(\rho)$  only when  $\partial^- F_0(\rho) = \emptyset$ .

*Proposition 5.* If  $F_0 : X \rightarrow \mathbb{R} \cup \{+\infty\}$  is an admissible functional and if  $F : X \rightarrow \mathbb{R} \cup \{+\infty\}$  is the Lieb functional, then

$$-v \in \partial^- F_0(\rho) \iff F_0(\rho) = F(\rho) \wedge -v \in \partial^- F(\rho). \quad (28)$$

*Proof.* Let us assume that  $-v \in \partial^- F_0(\rho)$ . From Eq. (27), we then have  $E(v) = F_0(\rho) + (v|\rho)$ . Substituting this result into Eq. (24), we then find that  $F(\rho) = F_0(\rho)$  and  $-v \in \partial^- F(\rho)$ . Conversely, if  $F(\rho) = F_0(\rho)$  and  $-v \in \partial^- F(\rho)$  hold, then we have  $E(v) = F_0(\rho) + (v|\rho)$  by Eq. (24), from which  $-v \in \partial^- F_0(\rho)$  follows by Eq. (27).  $\square$

### C. Constrained-search density functionals

So far, we have not established a connection between the minimizing densities in the Hohenberg–Kohn variation principle in Eq. (2) and the minimizing wave functions in the Rayleigh–Ritz variation principle in Eq. (1). For instance, we have not shown that each  $\rho \in \partial^+ E(v)$  is the ground-state density associated with some wave function  $\psi$ . Introducing a generic (abstract) constrained-search density functional, we consider in this section the relation between minimizers in the Hohenberg–Kohn and Rayleigh–Ritz variation principles.

Let  $S$  be a set with elements  $s$  called *states* and let  $d : S \rightarrow X$  be a map from  $S$  to the Banach space of densities  $X$ . The image

$$\rho_s = d(s) \quad (29)$$

is called the *density* of  $s$ . However, no physical meaning is attached to  $s \in S$  or to  $\rho \in X$  at this point; they are mathematical objects—for example,  $\rho$  may be a (current) density or a reduced density matrix, while  $s$  may be a pure state or a density matrix. As before,  $X'$  is the dual space of  $X$ , meaning that  $v \in X'$  if and only if  $v : X \rightarrow \mathbb{R}$  is a linear and continuous function. Thus, the pairing  $(v|\rho)$  is separately linear and continuous in  $v$  and  $\rho$ . We call  $v$  a *potential* but again no physical meaning is attached at present.

Assume next that, for every  $v \in X'$ , we are given a map  $\mathcal{E}_v : S \rightarrow \mathbb{R}$  of the form

$$\mathcal{E}_v(s) = \mathcal{E}_0(s) + (v|\rho_s), \quad (30)$$

where  $\mathcal{E}_0 : S \rightarrow \mathbb{R}$  is bounded below, meaning that there exists an  $M \in \mathbb{R}$  such that

$$\mathcal{E}_0(s) \geq M, \quad \forall s \in S. \quad (31)$$

We call  $\mathcal{E}_v(s)$  the *expectation value* of the total energy when the system is in the state  $s$  and influenced by the potential  $v$ . This setting covers all standard formulations of DFT and CDFT, including both pure-state and density-matrix formulations—in particular, we do not assume linearity of  $\mathcal{E}_0(s)$  and  $d(s)$  in  $s$ .

Next, define the *ground-state energy*  $E : X' \rightarrow \mathbb{R} \cup \{-\infty\}$  by the Rayleigh–Ritz variation principle

$$E(v) := \inf_{s \in S} \mathcal{E}_v(s) = \inf_{s \in S} (\mathcal{E}_0(s) + (v|\rho_s)). \quad (32)$$

Given that  $v$  couples to  $\rho_s$  only during minimization, it makes sense to define the *constrained-search functional*  $F_{CS} : X \rightarrow \mathbb{R} \cup \{+\infty\}$  as the map

$$F_{CS}(\rho) = \inf \{ \mathcal{E}_0(s) \mid s \mapsto \rho \}, \quad (33)$$

which takes the value  $+\infty$  whenever there is no  $s \in S$  with  $\rho_s = \rho$ . Combining Eqs. (32) and (33), we obtain the Hohenberg–Kohn variation principle

$$E(v) = \inf_{\rho \in X} (F_{CS}(\rho) + (v|\rho)). \quad (34)$$

This result proves the following:

*Proposition 6.* The constrained-search functional  $F_{CS}$  in Eq. (33) is an admissible density functional for the energy  $E$  in Eq. (32).

#### D. Characterization of ground states

Suppose that  $v \in X'$  is such that there exists  $s \in S$  for which the infimum in Eq. (32) is a minimum,

$$E(v) = \inf_{s'} \mathcal{E}_v(s') = \mathcal{E}_v(s), \quad (35)$$

meaning that there exists a *ground state*  $s \in \arg \min_{s'} \mathcal{E}_v(s')$  for  $v$ , where  $\arg \min_{s'} \mathcal{E}_v(s')$  is the subset of  $S$  containing all minimizers of  $\mathcal{E}_v$ . Let now  $v' \in X'$  be arbitrary and compute

$$\begin{aligned} E(v') &= \inf_{s' \in S} \mathcal{E}_{v'}(s') \leq \mathcal{E}_{v'}(s) = \mathcal{E}_0(s) + (v'|\rho_s) \\ &= \mathcal{E}_v(s) + (v' - v|\rho_s) = E(v) + (v' - v|\rho_s), \end{aligned} \quad (36)$$

where we have used Eqs. (30) and (35). We have thus proved the following proposition:

*Proposition 7.* If  $s \in S$  is a ground state for  $v$  in Eq. (30), then  $\rho_s$  is a supergradient of  $E$  in Eq. (32) at  $v$ ,

$$s \in \arg \min_{s'} \mathcal{E}_v(s') \implies \rho_s \in \partial^+ E(v). \quad (37)$$

The following proposition establishes an important relationship between ground states and subgradients of  $F_{CS}$ :

*Proposition 8.* Let  $F_{CS} : X \rightarrow \mathbb{R} \cup \{+\infty\}$  be constrained-search functional equation (33). If  $s$  is the ground state for some potential  $v \in X'$  with density  $\rho_s$ , then  $-v \in \partial^- F_{CS}(\rho_s)$ .

*Proof.* Let  $s' \in S$  with  $\rho_{s'} = \rho_s$ . According to Eq. (32), we then have

$$E(v) = \mathcal{E}_0(s) + (v|\rho_s) \leq \mathcal{E}_0(s') + (v|\rho_s). \quad (38)$$

Subtracting  $(v|\rho_s)$  from both sides, taking the infimum on the right-hand side, and using the definition in Eq. (33), we obtain

$$\mathcal{E}_0(s) \leq \inf_{s' \mapsto \rho_s} \mathcal{E}_0(s') = F_{CS}(\rho_s) \leq \mathcal{E}_0(s). \quad (39)$$

Thus, if there is a ground state  $s \in S$  for  $v \in X'$ , then

$$\begin{aligned} F_{CS}(\rho_s) + (v|\rho_s) &= \mathcal{E}_0(s) + (v|\rho_s) = \mathcal{E}_v(s) \\ &= E(v) \leq F_{CS}(\rho) + (v|\rho), \quad \forall \rho \in X. \end{aligned} \quad (40)$$

Rearranging, we obtain

$$F_{CS}(\rho) \geq F_{CS}(\rho_s) - (v|\rho - \rho_s), \quad \forall \rho \in X \quad (41)$$

demonstrating that  $-v \in \partial^- F_{CS}(\rho_s)$  and completing the proof.  $\square$

Conversely, does the subgradient relation  $-v \in \partial^- F_{CS}(\rho)$  imply that there exists a ground state  $s \mapsto \rho$ ? To answer this question affirmatively, we must assume that  $F_{CS}$  is *expectation valued*, defined as follows:

*Definition 1 (Expectation-valued constrained-search functional).* A constrained-search functional  $F_{CS}$  is called expectation valued if, for every  $\rho$  with  $F_{CS}(\rho) < +\infty$ , there exists an  $s_\rho \in S$  such that

$$F_{CS}(\rho) = \inf_{s \mapsto \rho} \mathcal{E}_0(s) = \mathcal{E}_0(s_\rho), \quad s_\rho \mapsto \rho. \quad (42)$$

In other words, if  $F_{CS}$  is expectation valued, then the infimum in Eq. (33) is a minimum if  $F_{CS}(\rho) < +\infty$ , implying that  $F_{CS}(\rho)$  is the expectation value  $\mathcal{E}_0(s)$  of some state  $s \mapsto \rho$ .

If  $F_{CS}$  is expectation valued, it follows immediately that

$$\begin{aligned} -v \in \partial^- F_{CS}(\rho) &\implies E(v) = F_{CS}(\rho) + (v|\rho) \\ &\implies E(v) = \mathcal{E}_0(s_\rho) + (v|\rho) = \mathcal{E}_v(s_\rho) \\ &\implies s_\rho \in \arg \min_{s'} \mathcal{E}_v(s') \end{aligned} \quad (43)$$

and, therefore, that there exists a ground state  $s \mapsto \rho$  of  $v$ . Summarizing, we have proved the following:

*Proposition 9.* Suppose that  $F_{CS} : X \rightarrow \mathbb{R} \cup \{+\infty\}$  is an expectation-valued constrained-search functional. Then, for each  $v \in X'$ , we have

$$s_\rho \in \arg \min_{s'} \mathcal{E}_v(s') \iff -v \in \partial^- F_{CS}(\rho) \implies \rho \in \partial^+ E(v). \quad (44)$$

*Remark.* Proposition 9 for an expectation-valued constrained-search functional should be compared with Proposition 4 for a general admissible density functional. Whereas, for a general admissible density functional  $F_{CS}$ , the condition  $E(v) = F_{CS}(\rho) + (v|\rho)$  does not imply the existence of a ground state  $s \mapsto \rho$ , this implication does hold for an *expectation-valued constrained-search functional*. Compare also with Proposition 3, where the admissible density functional is assumed to be convex and lower semi-continuous (i.e., the Lieb functional).

*Proposition 10.* Suppose that an expectation-valued constrained-search functional  $F_{CS} : X \rightarrow \mathbb{R} \cup \{+\infty\}$  is convex and lower semi-continuous so that  $F_{CS} = F$ . Then, for each  $v \in X'$ , we have

$$s_\rho \in \arg \min_{s'} \mathcal{E}_v(s') \iff -v \in \partial^- F_{CS}(\rho) \iff \rho \in \partial^+ E(v). \quad (45)$$

*Proof.* Combine Propositions 3 and 9.  $\square$

The *domain of subdifferentiability* of  $F_{CS}$  is set of densities at which  $F_{CS}$  is subdifferentiable,

$$\text{dom}(\partial^- F_{CS}) = \{\rho \in X | \partial^- F_{CS}(\rho) \neq \emptyset\}. \quad (46)$$

Proposition 9 then states that the domain of differentiability of an expectation-valued constrained-search functional is precisely the set of densities that are the ground-state densities for some potential,

$$\text{dom}(\partial^- F_{CS}) = \{\rho \in X | E(v) = \mathcal{E}_v(s_\rho) \text{ for some } v \in X'\}. \quad (47)$$

It is a general result of convex analysis that  $\text{dom}(\partial^- F_{CS})$  is dense in  $\text{dom}(F_{CS})$  if  $F_{CS}$  is convex and lower semi-continuous.<sup>9</sup> Since the Lieb functional  $F$  is convex and lower semi-continuous,  $\text{dom}(\partial^- F)$  is dense in  $\text{dom}(F)$ .

#### E. Continuity and differentiability of $E(v)$

We consider here conditions for differentiability of  $E : X' \rightarrow \mathbb{R} \cup \{-\infty\}$ . From Eq. (34), it follows that  $E$  is a concave and upper semi-continuous function. Upper semi-continuity is, however, a rather weak property. What is needed to make  $E$  continuous? It is a fact that a concave (convex) map over

a Banach space is continuous on the interior of its domain.<sup>9</sup> Hence, if we can show that  $E(v)$  is finite for every  $v \in X'$ , then the domain  $\text{dom}(E) = X'$  and continuity follows. The trick to show finiteness of  $E(v)$  in the context of standard DFT is to observe that  $s \mapsto \mathcal{V}_v(s) = \langle v | \rho_s \rangle$  is *relatively bounded with  $\mathcal{E}_0$ -bound smaller than one*, meaning that, for each  $v \in X'$ , there exist  $\epsilon \in (0, 1)$  and  $C_\epsilon \geq 0$  such that

$$|\mathcal{V}_v(s)| \leq \epsilon \mathcal{E}_0(s) + C_\epsilon, \quad \forall s \in S. \quad (48)$$

Assuming that  $\mathcal{V}_v$  is relatively bounded with  $\epsilon < 1$  and with no assumption on  $C_\epsilon$ , we obtain

$$\begin{aligned} \mathcal{E}_v(s) &= \mathcal{E}_0(s) + \mathcal{V}_v(s) \geq \mathcal{E}_0(s) - \epsilon \mathcal{E}_0(s) - C_\epsilon \\ &= (1 - \epsilon) \mathcal{E}_0(s) - C_\epsilon. \end{aligned} \quad (49)$$

Taking the infimum over  $s \in S$  and using the fact that  $\mathcal{E}_0(s)$  is by definition below bounded, we find

$$E(v) \geq (1 - \epsilon)M - C_\epsilon > -\infty. \quad (50)$$

*Proposition 11.* Let  $\mathcal{E}_0 : S \rightarrow \mathbb{R}$ ,  $E : X' \rightarrow \mathbb{R} \cup \{-\infty\}$ , and  $\mathcal{V}_v : S \rightarrow \mathbb{R}$  be as described above. If  $\mathcal{V}_v$  is relatively bounded with respect to  $\mathcal{E}_0$  with bound  $\epsilon < 1$  for each  $v \in X'$ , then  $E$  is continuous on  $X'$ .

*Proof.*  $E$  is everywhere finite, so  $\text{dom}(E) = X'$ . Therefore,  $E$  is continuous at any point  $v \in X'$ .  $\square$

Having determined sufficient conditions for continuity of  $E$ , what about differentiability? By definition,  $E$  is superdifferentiable at  $v \in X'$  if the superdifferential  $\partial^+ E(v)$  is non-empty. Clearly, if  $E$  is differentiable at  $v$ , the superdifferential is a singleton,  $\partial^+ E(v) = \{\nabla E(v)\}$ . The converse is, in general, almost true:<sup>9</sup>

**Theorem 1.** Let  $X$  be a Banach space. A convex (concave) map  $f : X \rightarrow \mathbb{R} \cup \{-\infty, +\infty\}$  is Gâteaux differentiable at  $x \in X$  if and only if it is continuous at  $x$  with a unique subgradient (supergradient).

Hence, a unique sub- or supergradient does not by itself guarantee continuity and therefore not (Gâteaux) differentiability: A subdifferential may be a singleton even if the function is non-differentiable. This subtle point illustrates the limitations of finite-dimensional intuition and has been the source of misunderstanding in the DFT literature. For a discussion, see Ref. 11 and references therein.

We can finally establish a useful statement on the differentiability of  $E : X' \rightarrow \mathbb{R} \cup \{-\infty\}$ :

*Proposition 12.* Let  $E : X' \rightarrow \mathbb{R}$  be everywhere finite and given by the Rayleigh–Ritz principle in Eq. (32) and assume that  $F_{\text{CS}}$  in Eq. (33) is expectation valued and equal to the Lieb functional (i.e., convex and lower semi-continuous). Then,  $E$  is differentiable at  $v$  if and only if all ground states  $s \in \text{argmin}_{s' \in S} \mathcal{E}_v(s')$  supported by  $v$  have the same ground-state density,  $s \mapsto \rho \in X$ . In particular,  $E$  is differentiable at  $v$  if there exists a unique ground state  $s$  for  $v$ .

*Proof.* Being continuous,  $E$  is differentiable at  $v$  if and only if  $\partial^+ E(v)$  is a singleton. But by Proposition 10,  $\partial^+ E(v)$  is a singleton if and only if all ground states of  $v$  have the same density, using the assumption that  $F_{\text{CS}}$  is the Lieb functional.  $\square$

*Remark.* The message here is that, given the Rayleigh–Ritz variation principle, it is not sufficient to know that a potential  $v \in X'$  has a unique ground-state density  $\rho = \rho_s$  to prove differentiability of  $E$  at  $v$ . To identify the unique supergradient  $\rho \in \partial^+ E(v)$  with a ground-state density,  $F_{\text{CS}}$  must be identical with the Lieb functional (convex and lower semi-continuous) and expectation valued. If the Lieb functional happens to be different from every possible constrained-search functional, differentiability may fail, even if  $v$  has a unique ground-state density  $\rho_s$ .

Starting from a Hohenberg–Kohn variation principle with an arbitrary admissible density functional, it seems hard to prove differentiability from the sole assumption that  $v$  has a unique ground-state density  $\rho_s$ . Identifying the proper constrained-search functional, based on the Rayleigh–Ritz variation principle, seems the only way out of the problem.

### III. APPLICATION TO DFT FOR MOLECULAR SYSTEMS

#### A. Ground states and ground-state densities

For  $N$ -electron systems, each normalized wave function has a density  $\rho \in L^1(\mathbb{R}^3)$  with  $\rho \geq 0$  almost everywhere and  $\int \rho(\mathbf{r}) \, d\mathbf{r} = N$ . The set of states  $S$  can be taken to be either the  $L^2$  normalized states  $\psi \in H_S^1(\mathbb{R}^{3N})$  (pure states) or the set of density matrices  $\Gamma = \sum_k \lambda_k |\psi_k\rangle\langle\psi_k|$  constructed as convex combinations from an orthonormal set  $\{\psi_k\} \subset H_S^1(\mathbb{R}^{3N})$  with  $\lambda_k \geq 0$  and  $\sum_k \lambda_k = 1$  (mixed states). In the pure-state and mixed-state cases, respectively, constrained search gives the functionals  $F_{\text{LL}}$  defined in Eq. (3) and  $F_{\text{DM}}$  defined in Eq. (4),

$$\begin{aligned} F_{\text{LL}}(\rho) &= \inf_{\psi \mapsto \rho} \mathcal{E}_0(\psi), \quad \mathcal{E}_0(\psi) = \langle \psi | \hat{T} + \hat{W} | \psi \rangle, \\ \mathcal{V}_v(\psi) &= \langle \psi | \hat{V} | \psi \rangle = (\rho_v | v), \end{aligned} \quad (51)$$

and

$$\begin{aligned} F_{\text{DM}}(\rho) &= \inf_{\Gamma \mapsto \rho} \mathcal{E}_0(\Gamma), \quad \mathcal{E}_0(\Gamma) = \text{Tr}[(\hat{T} + \hat{W})\Gamma], \\ \mathcal{V}_v(\Gamma) &= \text{Tr}(\Gamma \hat{V}) = (\rho_\Gamma | v), \end{aligned} \quad (52)$$

where  $\hat{V}$  is the multiplication operator associated with  $v$ . It is obvious that  $F_{\text{DM}} \leq F_{\text{LL}}$ . It is less obvious, but true, that there are  $\rho \in L^1$  for which  $F_{\text{DM}}(\rho) < F_{\text{LL}}(\rho)$ .

In a classic paper,<sup>13</sup> Kato demonstrated that, for each  $v \in L^2(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$ , the  $N$ -electron Hamiltonian  $\hat{H} = \hat{T} + \hat{W} + \hat{V}$  is self-adjoint on  $L^2(\mathbb{R}^{3N})$  with domain  $H_S^2(\mathbb{R}^{3N})$  and bounded below. More generally, Simon demonstrated that, for each  $v \in L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$  (which includes all Coulomb potentials),  $\mathcal{V}_v$  is relatively  $\mathcal{E}_0$ -bounded with an arbitrarily small bound.<sup>14</sup>

**Theorem 2.** Let  $v \in L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$  and let  $\hat{V}$  be the corresponding multiplication operator. Then, for any  $\epsilon > 0$ , there exists a constant  $C_\epsilon \geq 0$ , such that for all  $\psi \in H_S^1(\mathbb{R}^{3N})$  with  $\|\psi\|_2 = 1$ ,

$$|\langle \psi | \hat{V} | \psi \rangle| \leq \epsilon \langle \psi | \hat{T} + \hat{W} | \psi \rangle + C_\epsilon. \quad (53)$$

*Proof.* See Ref. 14.  $\square$

In the pure-state case, therefore, each  $v \in L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$  gives a  $\mathcal{V}_v$  relatively bounded by  $\mathcal{E}_0$ , with bound  $\epsilon$  arbitrarily small. Therefore,  $E(v)$  is continuous over  $L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$ , by Proposition 11.

Lieb proved that  $F_{LL}$  and  $F_{DM}$  are both expectation valued.<sup>4</sup> In the same publication, a proof (due to Simon) that  $F_{DM} : L^1(\mathbb{R}^3) \rightarrow \mathbb{R} \cup \{+\infty\}$  is convex and lower semi-continuous was given. Using the Sobolev embedding theorem, it can be shown that for each  $\psi \in H_S^1(\mathbb{R}^{3N})$ , the corresponding density  $\rho \leftarrow \psi$  belongs to  $L^3(\mathbb{R}^3)$ .<sup>4</sup> Thus, it is appropriate to consider the Banach space

$$X_L := L^1(\mathbb{R}^3) \cap L^3(\mathbb{R}^3) \quad (54)$$

with norm  $\|\cdot\| = \|\cdot\|_{L^1} + \|\cdot\|_{L^3}$ , whose dual space is

$$X'_L = L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3) \quad (55)$$

with the topology induced by  $\|\cdot\|$ .<sup>15</sup> Since convergence in  $X_L$  implies convergence in  $L^1$ ,  $F_{DM} : X_L \rightarrow \mathbb{R} \cup \{+\infty\}$  is lower semi-continuous as well. Applying Proposition 10 for  $F_{DM}$  (which is expectation valued and lower semi-continuous convex) and Proposition 9 for  $F_{LL}$  (which is expectation valued but not lower semi-continuous convex), we obtain the following:

*Corollary 1.* Let  $v \in X'_L = L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$ . Then,

$$\begin{aligned} \Gamma \in \arg \min_{\Gamma'} (\mathcal{E}_0(\Gamma') + (\rho_{\Gamma'}|v)) &\iff -v \in \partial^- F_{DM}(\rho_{\Gamma'}) \\ &\iff \rho_{\Gamma'} \in \partial^+ E(v), \end{aligned} \quad (56)$$

and

$$\begin{aligned} \psi \in \arg \min_{\psi'} (\mathcal{E}_0(\psi') + (\rho_{\psi'}|v)) &\iff -v \in \partial^- F_{LL}(\rho_{\psi'}) \\ &\implies \rho_{\psi'} \in \partial^+ E(v). \end{aligned} \quad (57)$$

Note that  $\rho \in \partial^+ E(v)$  does not imply the existence of a ground-state wave function for  $v$  such that  $\psi \mapsto \rho$ , only the existence of a mixed ground state  $\Gamma \mapsto \rho$ . For example, if  $v \in X'_L$  has a twofold degeneracy with pure ground states  $\psi_1$  and  $\psi_2$ , then  $\lambda\rho_1 + (1-\lambda)\rho_2 \in \partial^+ E(v)$  but there may be no pure ground state with this density. On the other hand,  $\lambda|\psi_1\rangle\langle\psi_1| + (1-\lambda)|\psi_2\rangle\langle\psi_2|$  is a mixed ground state with this density. We note that  $F_{DM}$  and  $E$  are subdifferential and superdifferentiable, respectively, on dense subsets of their domains.

A remark on representability is here in order. A density  $\rho$  is said to be *v-representable* if it is the density of some ground-state wave function  $\psi \mapsto \rho$ ; likewise,  $\rho$  is said to be *ensemble v-representable* if it is associated with some ground-state density matrix  $\Gamma \mapsto \rho$ . Letting  $\mathcal{A}_N$  and  $\mathcal{B}_N$  be the sets of all pure and ensemble ground-state densities in  $X$ , respectively, we conclude from Eq. (47) that

$$\mathcal{A}_N = \text{dom}(\partial^- F_{LL}), \quad \mathcal{B}_N = \text{dom}(\partial^- F_{DM}). \quad (58)$$

Moreover,  $\mathcal{B}_N$  is dense in  $\text{dom}(F_{DM})$  since  $F_{DM}$  is lower semi-continuous and convex.<sup>4</sup>

## B. Topology dependence of the Lieb functional

Recall that the Lieb functional  $F : X \rightarrow \mathbb{R} \cup \{+\infty\}$  depends explicitly on the Banach space  $X$ , including its topology.

We now demonstrate this using an explicit example. Motivated by the set inclusion

$$X_L = L^1(\mathbb{R}^3) \cap L^3(\mathbb{R}^3) \subset X_H := L^2(\mathbb{R}^3) \quad (59)$$

and the fact that  $X_H$  is Hilbert space with a simpler structure than the non-reflexive space  $X_L$ , it is tempting to consider  $F_{DM}$  as a function on  $X = X_H$ . However, the embedding  $X_L \subset X_H$  is not continuous: Convergence in  $X_L$  does not imply convergence in  $X_H$ . Even if  $F_{DM}$  is lower semi-continuous with respect to  $X_L$ , it may fail to be so in  $X_H$ . To see this, we note that, since  $X_H$  is a Hilbert space, the dual space is given by  $X'_H = X_H$ , which does not admit constant potentials: If  $v \in X_H$ , then the gauge-transformed potential  $v + c$  does not belong to  $X_H$ , for any constant  $c \neq 0$ . This observation allows us to prove the following result:

*Proposition 13.* For each  $v \in X_H$ , we have  $E(v) \leq 0$ . If  $v \geq 0$  almost everywhere, then  $E(v) = 0$ .

*Proof.* See the [Appendix](#). The proof is based on the following idea. Write  $v = v_+ - v_-$  where  $v_\pm \geq 0$  almost everywhere. The negative part  $v_-$  can only lower the energy, whereas  $v_+ \in X_H$  implies that  $v$  decays at infinity (in an average sense), thereby allowing the electrons to lower their energy to zero by “escaping to infinity.” Note how the fact that nonzero  $c \notin X_H$  affects this argument.  $\square$

Consider now  $\rho \equiv 0$ , for which  $F_{DM}(\rho) = +\infty$  since no  $\Gamma \mapsto 0$ . Evaluating the conjugate (Lieb) functional with respect to  $X_H$  at  $\rho = 0$ , we obtain

$$F(0) = \sup_{v \in X_H} (E(v) - (v|0)) = \sup_{v \in X_H} E(v) = 0. \quad (60)$$

Note that a different result is obtained using  $X_L$ , which admits constant potentials  $v(\mathbf{r}) \equiv c \in \mathbb{R}$ ,

$$\begin{aligned} F(0) &= \sup_{v \in X_L} (E(v) - (v|0)) \\ &= \sup_{v \in X_L} E(v) = +\infty = F_{DM}(0). \end{aligned} \quad (61)$$

As an immediate consequence, we arrive at the following result on  $X_H$ :

*Proposition 14.* For any  $v \in X_H$  such that  $v \geq 0$  almost everywhere, it holds that

$$E(v) = F(0) + (v|0) \wedge -v \in \partial^- F(0) \wedge 0 \in \partial^+ E(v), \quad (62)$$

where  $F$  is conjugate to  $E$ . There exists no ground state  $\psi \in H_S^1(\mathbb{R}^{3N})$  for any  $v \geq 0$ .

*Proof.* Eq. (62) follows from Proposition 3. It remains to show that there exists no ground state if  $v \geq 0$  almost everywhere. Since  $E(v) = 0$ , it is sufficient to show that, for each  $\psi \in H_S^1(\mathbb{R}^{3N})$ , it holds that  $\mathcal{E}_v(\psi) > 0$ . We have  $\mathcal{E}_v(\psi) \geq \langle \psi | \hat{T} | \psi \rangle$ . But if  $\psi$  has zero kinetic energy, then  $\nabla\psi = 0$ , from which it follows that  $\psi = 0$  almost everywhere, contradicting  $\|\psi\|_2 = 1$ . Thus,  $\mathcal{E}_v(\psi) \geq \langle \psi | \hat{T} | \psi \rangle > 0$ .  $\square$

Our discussion illustrates how the choice of Banach space  $X$  of densities affects the properties of the conjugate universal functional  $F : X \rightarrow \mathbb{R} \cup \{+\infty\}$ . Clearly, the Lieb functional

$F_{\text{DM}}$  for the space  $X_L$  is very different from the Lieb functional for  $X_H$ , since, in the latter case, for any non-negative potential  $v$ , the unphysical density  $\rho \equiv 0$  is a minimizer of the Hohenberg–Kohn variation principle. But  $v$  does not even have a ground state and certainly not a ground state with density  $\rho \equiv 0$ .

Connecting with the discussion following Proposition 12, we can see how topology influences differentiability of  $E$ . The map  $E : X_H \rightarrow \mathbb{R}$  is pointwise identical to  $E : X'_L \rightarrow \mathbb{R}$ : it is by definition the ground-state energy of the system in the external potential  $v$ , defined via the Rayleigh–Ritz variation principle. However, the topology on  $X_H$  is different and  $F_{\text{DM}}$  is no longer equal to the Lieb functional. We then cannot conclude from Proposition 12 that  $E : X_H \rightarrow \mathbb{R}$  is differentiable at  $v$  if  $v \in X_H$  has a unique ground state.

#### IV. APPLICATION TO CDFT FOR MOLECULAR SYSTEMS IN MAGNETIC FIELDS

Consider an  $N$ -electron system subject to an external magnetic vector potential  $\mathbf{A} : \mathbb{R}^3 \rightarrow \mathbb{R}^3$ , with associated magnetic field  $\mathbf{B}(\mathbf{r}) = \nabla \times \mathbf{A}(\mathbf{r})$  (in the distributional sense). Considering  $\mathbf{A}$  as a variable on the same footing as the scalar potential  $v$ , we arrive at CDFT, where the paramagnetic current density

$\mathbf{j}_p \in \mathbf{L}^1(\mathbb{R}^3)$  appears as a variable together with  $\rho$ .<sup>6,8,16</sup> The mathematical foundation of CDFT is not as well developed as that of DFT. Indeed, part of the motivation for the present work stems from a study of CDFT. On the other hand, Laestadius<sup>8</sup> has taken important steps—proving, for example, Proposition 17 below.

Following Ref. 8, we assume for simplicity that the components of  $\mathbf{A}$  are  $L^\infty(\mathbb{R}^3)$  functions. The single-electron momentum operator  $-i\nabla$  is then replaced by  $-i\nabla + \mathbf{A}$ , transforming the  $N$ -electron kinetic-energy operator  $\hat{T}$  into the corresponding  $\hat{T}_\mathbf{A}$ . Since  $\mathbf{A} \in \mathbf{L}^\infty(\mathbb{R}^3)$ , the kinetic-energy expectation value is still well defined for each  $\psi \in H_S^1(\mathbb{R}^{3N})$ . In terms of the density  $\rho \in L^1(\mathbb{R}^3)$  and the paramagnetic current density  $\mathbf{j}_p \in \mathbf{L}^1(\mathbb{R}^3)$ , we obtain

$$\langle \psi | \hat{T}_\mathbf{A} | \psi \rangle = \langle \psi | \hat{T} | \psi \rangle + \frac{1}{2} \int |\mathbf{A}(\mathbf{r})|^2 \rho(\mathbf{r}) \, d\mathbf{r} + \int \mathbf{A}(\mathbf{r}) \cdot \mathbf{j}_p(\mathbf{r}) \, d\mathbf{r}. \quad (63)$$

The ground-state energy is thus given by

$$E(v, \mathbf{A}) = \inf_{\psi, \|\psi\|_2=1} \langle \psi | \hat{T}_\mathbf{A} + \hat{W} + \hat{V} | \psi \rangle \\ = \inf_{(\rho, \mathbf{j}_p)} (F_{\text{VR}}(\rho, \mathbf{j}_p) + (v + \frac{1}{2}A^2|\rho) + (\mathbf{A}|\mathbf{j}_p)), \quad (64)$$

where we have introduced the *VR functional*<sup>6</sup>

$$F_{\text{VR}}(\rho, \mathbf{j}_p) := \inf \{ \langle \psi | \hat{T} + \hat{W} | \psi \rangle \mid \psi \in H_S^1(\mathbb{R}^{3N}), \|\psi\|_2 = 1, \psi \mapsto (\rho, \mathbf{j}_p) \}. \quad (65)$$

Similarly, we may define a density-matrix constrained-search functional

$$F_{\text{DM}}(\rho, \mathbf{j}_p) = \inf \{ \text{Tr}((\hat{T} + \hat{W})\Gamma) \mid \Gamma \mapsto (\rho, \mathbf{j}_p) \}, \quad (66)$$

where  $\rho_\Gamma = \sum_k p_k \rho_{\psi_k}$  and  $\mathbf{j}_{p\Gamma} = \sum_k p_k \mathbf{j}_{p\psi_k}$ . Although  $F_{\text{DM}}$  is convex by construction, the presence of the nonlinear  $\mathbf{A}$ -dependent term makes  $E(v, \mathbf{A})$  nonconcave. Following Ref. 16, it is therefore natural instead to work with  $\tilde{E}(u, \mathbf{A}) = E(u - \frac{1}{2}A^2, \mathbf{A})$ , defined in Proposition 16 below. We note that

$$(\rho, \mathbf{j}_p) \in X_L \times \mathbf{L}^1(\mathbb{R}^3), \quad (67)$$

where  $X_L \times \mathbf{L}^1(\mathbb{R}^3)$  is a Banach space with norm  $\|(\rho, \mathbf{j}_p)\| = \|\rho\| + \|\mathbf{j}_p\|_{\mathbf{L}^1}$  and dual  $X'_L \times \mathbf{L}^\infty(\mathbb{R}^3)$ , the latter containing all  $(v, \mathbf{A})$ .

First, we prove finiteness of the ground-state energy:

*Proposition 15.* For every  $(v, \mathbf{A}) \in X_L \times \mathbf{L}^\infty$ , the ground-state energy is finite,  $E(v, \mathbf{A}) > -\infty$ .

*Proof.* For an  $N$ -electron system influenced by a magnetic field, the *diamagnetic inequality*<sup>17</sup> gives

$$\langle \phi | \hat{T} | \phi \rangle \leq \langle \psi | \hat{T}_\mathbf{A} | \psi \rangle, \quad \forall \psi \in H_S^1(\mathbb{R}^{3N}), \quad (68)$$

where  $\phi = |\psi|$  be the pointwise absolute value. Next, using the identity  $\rho_\psi = \rho_\phi$  and the relative boundedness of  $v \in X_L$  with respect to  $\hat{T}$ , we find that  $\hat{V}$  is relatively bounded with respect to  $\hat{T}_\mathbf{A}$ ,

$$|\langle \psi | \hat{V} | \psi \rangle| = |\langle \phi | \hat{V} | \phi \rangle| \leq \epsilon \langle \phi | \hat{T} | \phi \rangle + C_\epsilon \leq \epsilon \langle \psi | \hat{T}_\mathbf{A} | \psi \rangle + C_\epsilon. \quad (69)$$

Similarly,  $\hat{W}$  is relatively bounded with respect to  $\hat{T}_\mathbf{A}$ . It follows that  $\langle \psi | \hat{H} | \psi \rangle$  is below bounded, and thus that  $E(v, \mathbf{A}) > -\infty$ .  $\square$

Next, we note that, for each  $\mathbf{A} \in \mathbf{L}^\infty(\mathbb{R}^3)$ , we have  $|\mathbf{A}|^2 \in L^\infty(\mathbb{R}^3) \subset X'_L$ . Therefore, for each pair  $(v, \mathbf{A}) \in X_L$ , we have  $(v \pm \frac{1}{2}|\mathbf{A}|^2, \mathbf{A}) \in X_L \times \mathbf{L}^\infty$ , making the following proposition easy to prove:

*Proposition 16.* If  $F_0 : X_L \times \mathbf{L}^1$  is either  $F_{\text{VR}}$  or  $F_{\text{DM}}$ , then  $\tilde{E} : X'_L \times \mathbf{L}^\infty(\mathbb{R}^3) \rightarrow \mathbb{R}$  defined by

$$\tilde{E}(u, \mathbf{A}) = \inf_{(\rho, \mathbf{j}_p)} (F_0(\rho, \mathbf{j}_p) + (u|\rho) + (\mathbf{A}|\mathbf{j}_p)) \quad (70)$$

is concave, finite, and therefore continuous. The ground-state energies  $E$  and  $\tilde{E}$  are related by

$$E(v, \mathbf{A}) = \tilde{E}(v + \frac{1}{2}|\mathbf{A}|^2, \mathbf{A}), \quad \tilde{E}(u, \mathbf{A}) = E(u - \frac{1}{2}|\mathbf{A}|^2, \mathbf{A}). \quad (71)$$

*Proof.* We leave the details to the reader.  $\square$

The map  $(v, \mathbf{A}) \mapsto (v + \frac{1}{2}|\mathbf{A}|^2, \mathbf{A})$  defined on  $X'_L \times \mathbf{L}^\infty(\mathbb{R}^3)$  is smooth and invertible, with smooth inverse  $(u, \mathbf{A}) \mapsto (u - \frac{1}{2}|\mathbf{A}|^2, \mathbf{A})$ . Thus, the properties of  $E$  are reflected in properties  $\tilde{E}$  and vice versa. If  $F_0$  is an admissible functional for  $\tilde{E} : X'_L \times \mathbf{L}^\infty \rightarrow \mathbb{R}$ , then

$$E(v, \mathbf{A}) = F_0(\rho, \mathbf{j}_p) + (v + \frac{1}{2}|\mathbf{A}|^2|\rho) + (\mathbf{A}|\mathbf{j}_p) \\ \iff -(v + \frac{1}{2}|\mathbf{A}|^2, \mathbf{A}) \in \partial^- F_0(\rho, \mathbf{j}_p) \\ \implies (\rho, \mathbf{j}_p) \in \partial^+ \tilde{E}(v + \frac{1}{2}|\mathbf{A}|^2, \mathbf{A}). \quad (72)$$

Laestadius proved the following result:<sup>8</sup>

*Proposition 17.*  $F_{\text{VR}} : L^1(\mathbb{R}^3) \times \mathbf{L}^1(\mathbb{R}^3) \rightarrow \mathbb{R} \cup \{+\infty\}$  is expectation valued.

Proposition 9, therefore, gives

$$\begin{aligned} \psi_\rho \in \arg \min_{\psi'} \langle \psi | \hat{H} | \psi \rangle \\ \iff E(v, \mathbf{A}) = F_{\text{VR}}(\rho, \mathbf{j}_p) + (v + \frac{1}{2}|\mathbf{A}|^2|\rho) + (\mathbf{A}|\mathbf{j}_p). \end{aligned} \quad (73)$$

Thus, with the Vignale–Rasolt functional and the space  $X_L \times \mathbf{L}^1$  as density space, there are no minimizers of the pure-state Hohenberg–Kohn variation principle for CDFT that do not correspond to ground-state wave functions.

On the other hand, it is not known whether the density-matrix functional  $F_{\text{DM}}$  in (65) is expectation valued, but it seems likely. If  $F_{\text{DM}}$  is not expectation valued, there may be  $(\rho, \mathbf{j}_p)$  such that

$$E(v, \mathbf{A}) = F_{\text{DM}}(\rho, \mathbf{j}_p) + (v + \frac{1}{2}|\mathbf{A}|^2|\rho) + (\mathbf{A}|\mathbf{j}_p) \quad (74)$$

for which no  $\Gamma \mapsto (\rho, \mathbf{j}_p)$ , meaning that  $(\rho, \mathbf{j}_p)$  is an unphysical minimizer of the density-matrix Hohenberg–Kohn variation principle for CDFT.

Neither is it known whether  $F_{\text{DM}}$  is lower semi-continuous in the  $L^1 \times \mathbf{L}^1$  topology; the proof for the ordinary DFT case in Ref. 4 is not easily generalized to the present situation. Thus, there could be  $(\rho, \mathbf{j}_p) \in \partial^+ \tilde{E}(v + \frac{1}{2}|\mathbf{A}|^2, \mathbf{A})$  such that  $-(v + \frac{1}{2}|\mathbf{A}|^2, \mathbf{A}) \notin \partial^- F_{\text{DM}}(\rho, \mathbf{j}_p)$ , so that  $(\rho, \mathbf{j}_p)$  does not satisfy Eq. (74).

Finally, we may consider the Lieb functional  $F : X_L \times \mathbf{L}^1 \rightarrow \mathbb{R} \cup \{+\infty\}$ , defined as

$$\begin{aligned} F(\rho, \mathbf{j}_p) &:= \sup_{u, \mathbf{A}} (\tilde{E}(u, \mathbf{A}) - (u|\rho) - (\mathbf{A}|\mathbf{j}_p)) \\ &= \sup_{v, \mathbf{A}} (E(v, \mathbf{A}) - (v + \frac{1}{2}|\mathbf{A}|^2|\rho) - (\mathbf{A}|\mathbf{j}_p)). \end{aligned} \quad (75)$$

This functional is convex and lower semi-continuous by construction. However, unlike in standard DFT, it is unknown whether  $F(\rho, \mathbf{j}_p) = F_{\text{DM}}(\rho, \mathbf{j}_p)$ .

From the perspective of applying Proposition 10, thereby establishing a result like Corollary 1 for CDFT, we must establish that  $F_{\text{DM}}$  is both expectation valued and lower semi-continuous. At present, therefore, we do not know if  $E(v, \mathbf{A})$  is Gâteaux differentiable when the ground-state density  $(\rho, \mathbf{j}_p)$  is unique.

## V. CONCLUSION

We have analyzed the relationship between ground-state densities obtained from the Rayleigh–Ritz variation principle (by minimizing over pure-state wave functions or mixed-state density matrices) and from the Hohenberg–Kohn variation principles (by minimizing over densities using an admissible density functional  $F_0(\rho)$ ). In particular, we have established some basic results for admissible density functionals. The central result is Proposition 4, stating that

$$E(v) = F_0(\rho) + (v|\rho) \iff -v \in \partial^- F_0(\rho) \implies \rho \in \partial^+ E(v) \quad (76)$$

holds for all admissible density functionals  $F_0$ . For the convex lower semi-continuous Lieb functional  $F$ , the stronger Proposition 3 holds

$$E(v) = F(\rho) + (v|\rho) \iff -v \in \partial^- F(\rho) \iff \rho \in \partial^+ E(v). \quad (77)$$

General admissible functionals do not have an *a priori* connection with the Rayleigh–Ritz variation principle—that is, with minimization over *physical states*. We, therefore, introduced the particular class of admissible density functionals called *constrained-search functionals*, defined via the Rayleigh–Ritz variation procedure and the formula  $F_{\text{CS}}(\rho) = \inf_{s \mapsto \rho} \mathcal{E}_0(s)$ , where  $s$  can be a wave function or a density matrix, depending on the context. The concept of *expectation valuedness* of  $F_{\text{CS}}$  allowed us to make a connection between minimizers in the Hohenberg–Kohn variation principle and minimizers of the Rayleigh–Ritz variation principle. In particular, Proposition 9 states that

$$s_\rho \in \arg \min_{s'} \mathcal{E}_v(s') \iff -v \in \partial^- F_{\text{CS}}(\rho) \implies \rho \in \partial^+ E(v). \quad (78)$$

If in addition to being expectation valued,  $F_{\text{CS}}$  is convex and lower semicontinuous, Proposition 10 gives us

$$s_\rho \in \arg \min_{s'} \mathcal{E}_v(s') \iff -v \in \partial^- F_{\text{CS}}(\rho) \iff \rho \in \partial^+ E(v). \quad (79)$$

Thus, under these conditions, a minimizer in the Hohenberg–Kohn variation principle is equivalent to a minimizer in the Rayleigh–Ritz variation principle. In our discussion, the role of the chosen topology of the underlying density space  $X$  was made clear. If the topology changes, the rightmost equivalence in Eq. (79) may be broken, admitting minimizing densities  $\rho \in X$  in the Hohenberg–Kohn variation principle that are not associated with any physical state of the system.

Within the framework of standard DFT for molecular systems with  $v \in L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$ , a one-to-one correspondence between the mixed ground-state densities of the Rayleigh–Ritz variation principle and the mixed ground-state densities of the Hohenberg–Kohn variation principle with the Lieb density-matrix constrained-search functional  $F_{\text{DM}} : L^1(\mathbb{R}^3) \cap L^3(\mathbb{R}^3) \rightarrow \mathbb{R} \cup \{+\infty\}$  was established,

$$\begin{aligned} \Gamma \in \arg \min_{\Gamma'} (\mathcal{E}_0(\Gamma') + (\rho_\Gamma|v)) \iff -v \in \partial^- F_{\text{DM}}(\rho_\Gamma) \\ \iff \rho_\Gamma \in \partial^+ E(v). \end{aligned} \quad (80)$$

A similar one-to-one correspondence exists between the pure ground-state densities of the Rayleigh–Ritz variation principle and the pure ground-state densities of the Hohenberg–Kohn variation principle with the Levy–Lieb functional  $F_{\text{LL}} : L^1(\mathbb{R}^3) \cap L^3(\mathbb{R}^3) \rightarrow \mathbb{R}$ ,

$$\begin{aligned} \psi \in \arg \min_{\psi'} (\mathcal{E}_0(\psi') + (\rho_\psi|v)) \iff -v \in \partial^- F_{\text{LL}}(\rho_\psi) \\ \implies \rho_\psi \in \partial^+ E(v). \end{aligned} \quad (81)$$

In other words, all physical ground-state densities (pure or mixed) are recovered with these functionals and there are no false densities (i.e., minimizing densities not associated with a ground-state wave function).

The topology of the underlying Banach space  $X$  impinges on the results—in particular, we noted that the Lieb functional  $F : X \rightarrow \mathbb{R} \cup \{+\infty\}$  depends explicitly on  $X$ . As an illustration,  $F \neq F_{\text{DM}}$  on  $X = L^2(\mathbb{R}^3)$  but  $F = F_{\text{DM}}$  on  $L^1(\mathbb{R}^3) \cap L^3(\mathbb{R}^3)$ . Finally, CDFT was discussed and some open problems were pointed out—for example, it is unknown whether or not  $F_{\text{DM}}(\rho, \mathbf{j}_p)$  is lower semi-continuous in any useful topology such as  $L^1(\mathbb{R}^3) \times \mathbf{L}^1(\mathbb{R}^3)$ .

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## APPENDIX: PROOF OF PROPOSITION 13

*Proof of Proposition 13.* Writing  $v = v_+ - v_-$ , we obtain

$$\begin{aligned} E(v) &= \inf_{\rho} (F_{\text{DM}}(\rho) + (v_+|\rho) - (v_-|\rho)) \\ &\leq \inf_{\rho} (F_{\text{DM}}(\rho) + (v_+|\rho) = E(v_+)). \end{aligned} \quad (\text{A1})$$

It is, therefore, sufficient to show that  $E(v_+) \leq 0$ . In fact, we show that  $E(v_+) = 0$ .

Let  $v \geq 0$  almost everywhere. Let  $\lambda > 0$  be arbitrary and let  $\Omega_{k,\lambda}$  with  $k \in \mathbb{N}$  be disjoint cubes of side length  $\lambda$  such that  $\cup_k \Omega_{k,\lambda} = \mathbb{R}^3$ . Each  $\Omega_{k,\lambda}$  can be obtained by translation of  $\Omega_{1,\lambda}$ . Since  $v \in L^2(\mathbb{R}^3)$ ,

$$\int_{\mathbb{R}^3} v(\mathbf{r})^2 \, d\mathbf{r} = \sum_k \int_{\Omega_{k,\lambda}} v(\mathbf{r})^2 \, d\mathbf{r} < +\infty, \quad (\text{A2})$$

implying that  $\int_{\Omega_{k,\lambda}} v(\mathbf{r})^2 \, d\mathbf{r} \rightarrow 0$  as  $k \rightarrow \infty$ . Let  $\psi \in C_c^\infty(\mathbb{R}^{3N})$  be arbitrary but with support in  $\Omega_{1,\lambda}^N$  so that  $\rho_\psi \in C_c^\infty(\mathbb{R}^3)$  has support contained in  $\Omega_{1,\lambda}$ . By translating  $\psi$  properly (denoting the result by  $\psi_k$ ), the support of  $\psi_k$  is inside  $\Omega_{k,\lambda}^N$  and

$$F_{\text{DM}}(\rho_{\psi_k}) = F_{\text{DM}}(\rho_\psi) \leq \langle \psi | T + W | \psi \rangle \equiv \langle T \rangle + \langle W \rangle, \quad (\text{A3})$$

independent of  $k$ . We obtain

$$E(v) \leq \lim_k \left( \langle T \rangle + \langle W \rangle + \int_{\Omega_{k,1}} v(\mathbf{r}) \rho_k(\mathbf{r}) \, d\mathbf{r} \right) = \langle T \rangle + \langle W \rangle, \quad (\text{A4})$$

where we have used the fact that

$$\int_{\Omega_{k,1}} v(\mathbf{r}) \rho_k(\mathbf{r}) \, d\mathbf{r} \leq \left( \int_{\Omega_{k,1}} v(\mathbf{r})^2 \, d\mathbf{r} \right)^{1/2} \|\rho\|_2 \rightarrow 0 \quad (\text{A5})$$

as  $k \rightarrow \infty$ .

We now increase the size of the boxes  $\Omega_{k,\lambda}$  by varying  $\lambda > 0$ . By dilating  $\psi$  in the manner

$$\psi(\mathbf{r}_1, \dots) \mapsto \lambda^{3N/2} \psi(\lambda \mathbf{r}_1, \dots), \quad (\text{A6})$$

the support is still inside  $\Omega_{1,\lambda}^\infty$  and the density is scaled as  $\rho_\psi(\mathbf{r}) \rightarrow \lambda^{-3} \rho_\psi(\lambda^{-1} \mathbf{r})$ , conserving the number of particles. We obtain the scaling

$$\langle T \rangle + \langle W \rangle \rightarrow \lambda^{-2} \langle T \rangle + \lambda^{-1} \langle W \rangle. \quad (\text{A7})$$

By repeating the above argument for  $\lambda = 1$  and letting  $\lambda \rightarrow \infty$ , we obtain  $E(v) \leq 0$ . On the other hand,  $E(v) \geq 0$  since the Hamiltonian  $H(v)$  is positive with  $v \geq 0$ , yielding  $E(v) = 0$ .  $\square$

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